Recent Developments in O_2 Activation by Heterobimetallic Complexes

Claire Schmit Literature Seminar August 13th, 2020

The activation of dioxygen (O_2) is a key step in many metabolic and biosynthetic processes required for aerobic life, as well as for the reduction half-reaction for fuel cells and other energy technologies.[1] Dioxygen activation by metalloenzymes occurs when O_2 binds at the active sites, and generates a highly reactive intermediate which then oxidizes various biological substrates. In nature the activation of small molecules is often performed by enzymes with active sites that have several redox-active centers, where stability and reactivity can be modulated by redox-inactive Lewis-acidic metal ions.[4]

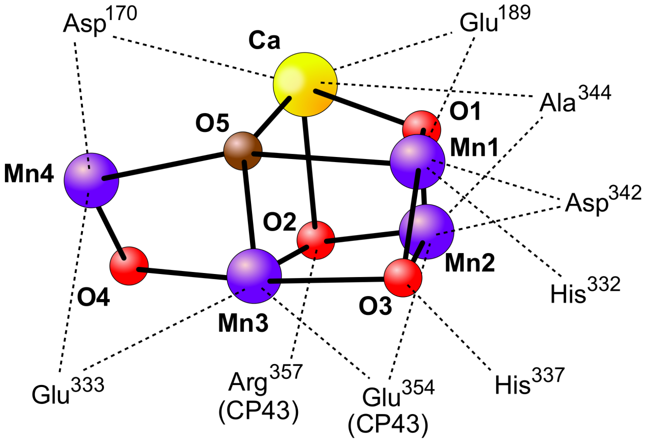

Figure 1. The metalloenzyme core of the oxygen-evolving center (OEC) of Photosystem II is made up of manganese ions (purple), calcium ion (yellow), and oxygen atoms (red).[2,3]

One well-known multimetallic system is the oxygen-evolving center (OEC) in Photosystem II, where manganese and calcium ions are bridged by oxygen ions, and this cluster converts two water molecules into O_2 gas and hydrogen ions.[2] The presence of the redox-inactive Lewis-acidic Ca^{2+} ion is known to be crucial for proper functioning,[4] which led to biomimetic systems that incorporate Lewis-acidic metal ions in their heterobimetallic design. This was found to increase the rate of O_2 activation in several systems,[5,8] supporting the idea that heterobimetallic complexes can take advantage of metal-metal cooperativity and activate substrates bifunctionally.[5,6] Most dinuclear complexes that activate O_2 catalytically are homometallic, but there is interest in heterobimetallic complexes because such compounds have shown unique reactivity and selectivity that differs from their monometallic analogues.[7] This change in reactivity is thought to be caused by the metal-metal interactions due to the enforced proximity of the two metal centers.[4]

Three ligand scaffolds used to construct heterobimetallic complexes include tripodal ligands,[8] siloxide ligands,[4] and a tris-(phosphinoamide) ligand framework.[10] Each type of ligand scaffold can produce heterobimetallic complexes, and these can then react with O_2 to form oxo- or peroxo-species, which are thought to be the key intermediates in O_2 activation that oxidize substrates for biological or industrial purposes. An example of a tripodal heterobimetallic complex from the Borovik group incorporates manganese and calcium into a monomeric hydroxo complex, proposed to be the result of the reaction between a heterobimetallic intermediate and O_2. The rate of this reaction was enhanced by the presence of redox-inactive metal ions Ca^{2+} or Ba^{2+}, leading to the hypothesis that the reduction to superoxide could be dependent on the prior formation of a heterobimetallic Mn/Ca complex that coordinates to dioxygen, and then facilitates the electron transfer. The activity of this hydroxo complex was not investigated further, so it is unknown it this could oxidize a substrate catalytically, or even at all.

To investigate the reactivity of heterobimetallic complexes with Lewis-acidic metal ions as integral parts of the ligand scaffold, the Limberg group added Li^+ ions into a siloxide ligand framework around a central chromium atom.[4] The Cr/Li heterobimetallic compound reacts with O_2 to form a superoxide complex, however this does not react further to oxidize external substrates. This was explained by the inaccessible superoxide ligand, as it was shielded by the ligands' phenyl residues.[10] In order to overcome the lack of reactivity with this Cr/Li compound, the Limberg group swapped out the lithium cations for zinc, which had a more accessible superoxide moiety and was moderately more reactive.[4]

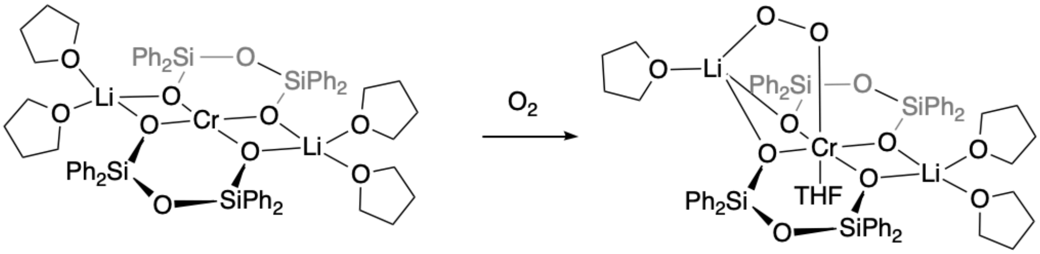

Figure 2. Reaction scheme showing the formation of a superoxide complex from the reaction of O_2 and a chromium(II) siloxide heterobimetallic.[10]

The incorporation of Lewis-acidic redox-inactive metal ions is thought to accelerate the rate of O_2 activation by facilitating substrate binding, while the transition metal still does the redox chemistry. However, the Thomas group took a different organizational approach by combining a late transition metal fragment that acts solely as the source of reducing equivalents with a redox-inactive early transition-metal.[9] The substrate binding, which occurs at the zirconium atom, is separate from the cobalt center that serves as a two-electron reductant. The Zr peroxo compound formed from the reaction of the Zr/Co heterobimetallic complex with O_2 was found to be highly reactive, and to possibly decompose through radical pathways involving the solvent.

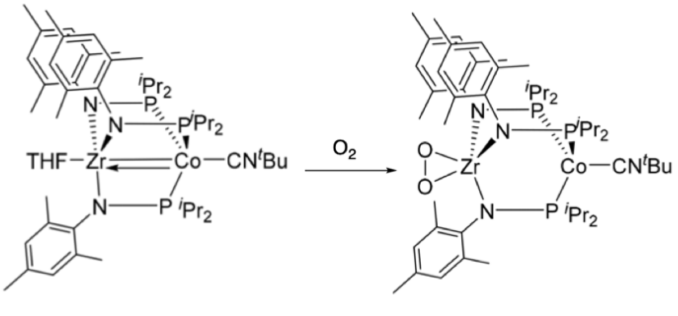

Figure 4. The reaction of a Zr/Co complex with O_2 makes a side-on peroxo species.[9]

Although nature can activate O_2 catalytically, new heterobimetallic compounds only do so stoichiometrically. Metal cooperativity and heterobimetallic compounds have made little progress in the problem of catalytic O_2 activation, however the separation of substrate binding from redox chemistry provides an interesting approach to new complex design within the field. Despite these developments, heterobimetallic compounds based on the goal of metal-metal cooperativity may not be the best solution to the problem of catalytic dioxygen activation, as these heterobimetallic complexes often activate O_2 only once.

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